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GLASS TANK REFRACTORIES AND THEIR CHEMICAL RELATIONSHIP WITH THE MOLTEN GLASS

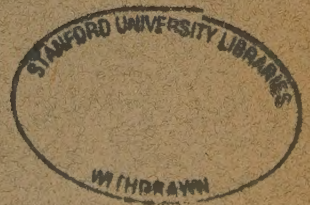
By
KAI-CHING LU

DISSERTATION

*Presented in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in the Graduate
School of the Ohio State University.*

✓
THE ENGINEERING EXPERIMENT STATION
BULLETIN NO. 44

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THE OHIO STATE UNIVERSITY
COLUMBUS



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Dissertation

THE purpose of the Engineering Experiment Station of Ohio State University, to quote from the act for its establishment, is "to make technical investigations and to supply engineering data which will tend to increase the economy, efficiency, and safety of the manufacturing, mineral, transportation and other engineering and industrial enterprises of the state and to promote the conservation and utilization of its resources."

The Engineering Experiment Station is for the service and assistance of the industries and people of Ohio in solving their technical problems. The Director of the Station and the members of the Advisory Council are selected from the faculty of the College of Engineering, The Ohio State University, and other members of the faculty are encouraged to undertake and direct research in their respective fields. Trained investigators devote their whole time to the solution of special problems. Besides the large testing machines and special apparatus in the Experiment Station Building, the research equipment comprises the laboratories of the various engineering departments. In addition the experimental brick plant at Roseville provides opportunity for practical investigation of all phases of heavy clay products manufacture.

The results of studies and researches are published in technical periodicals and are issued as bulletins and circulars of the Station. A list of the publications to date is given on the back cover of this bulletin.

Cooperation with industries in research which may be published for general benefit increases the usefulness of the Station and is desired. A very satisfactory form of such cooperation is the maintenance of graduate fellowships, the stipend of the fellow being paid either in whole or in part by the individuals or organizations cooperating. Inquiries regarding any phase of the work of the Station should be addressed to

THE DIRECTOR

Engineering Experiment Station
The Ohio State University
Columbus, Ohio

THE OHIO STATE UNIVERSITY
THE ENGINEERING EXPERIMENT STATION

BULLETIN No. 44

JULY, 1928

GLASS TANK REFRACTORIES AND
THEIR CHEMICAL RELATIONSHIP
WITH THE MOLTEN GLASS

By
KAI-CHING LU

Joint Cooperative Glass Fellow, 1927-1928
The Ohio State University

THE OHIO STATE UNIVERSITY
COLUMBUS

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ENGINEERING EXPERIMENT STATION BUILDING
THE OHIO STATE UNIVERSITY

The Engineering Experiment Station building will span the north end of the engineering quadrangle. The picture shows the completed portion, a four-story steel-framed structure about one-fifth the size of the proposed building. It is 103 by 134 feet overall, and contains approximately 40,000 square feet of floor space.

At present the building has the following uses:

- Top Floor: Ohio Stream Flow Survey, geodetic engineering offices and computing rooms, drain tile research.
- Third Floor: Cooperative Soil Research laboratory, gas laboratory, concrete research.
- Second Floor: Administrative offices of the Engineering Experiment Station, Ohio State Highway Testing laboratory.
- First Floor: Cement laboratory, coal and coke laboratory, timber treatment laboratory, large testing machines, fire-test furnace.

The testing machine room is 100x40 feet and the full height of the building. It contains a 10-ton crane.

Equipment and space are available for research in practically all fields of engineering. There are three large testing machines: a million pound compression-tension machine, a 500,000-lb. column machine, a 400,000-lb. beam machine. The fire test furnace will receive 10 ft. by 10 ft. wall sections. The retort for the gas laboratory is full size, having a capacity of one ton.

FOREWORD

The Federal Glass Company of Columbus, Ohio, and the Findlay Clay Products Company of Washington, Pennsylvania, wanted to find the answers to certain perplexing problems connected with the business of making glass. The Engineering Experiment Station at Ohio State University had laboratory facilities for making an investigation of these problems. An agreement was made that these companies would cooperate with the Engineering Experiment Station in a fellowship, the companies paying the stipend of the fellow, the Station contributing its laboratory facilities and supervision of the work.

Kai-Ching Lu, who was selected as the fellow, had received his Master of Science degree in 1925, and was continuing his studies. Arrangements were made for the glass research to count as part of the work for the Doctor of Philosophy degree which he received in June, 1928.

The results obtained in this cooperative investigation were entirely satisfactory to the donors of the fellowship, and were reported in Mr. Lu's doctor's thesis. To make these results available for glass technologists and others interested, the thesis has been published as this bulletin of the Engineering Experiment Station.

E. A. HITCHCOCK, *Director.*

GLASS TANK REFRACTORIES AND THEIR CHEMICAL RELATIONSHIP WITH THE MOLTEN GLASS

The corrosion of tank blocks by glass has attracted considerable attention in the past few years. The deterioration of refractories in this case is by no means a result of simple chemical reaction. The refractory is exposed at a high temperature to a molten silicate which is chemically very active and not dissimilar in composition to the refractory. The blocks also have to carry the weight of the upper part of the furnace and the crown of the tank and in addition must resist the thrust of the molten glass. Also the resistance of the blocks to corrosion is not a simple matter. The mineralogical constitution, porosity, uniformity and fineness of texture of the block, composition of the glass and the working temperature of the furnace are all influencing factors in deciding the life of the block in service.

The present investigation was undertaken to determine by chemical and microscopic analysis the composition and constitution of glass tank refractories, to isolate the different constituents present and to study each separately, and finally to apply the information so obtained in an examination of tank blocks which have been in service in order to ascertain the cause and the stages of destruction. Since the discovery of mullite and its identification as the stable compound in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system, considerable research has been carried on with satisfactory results. Mullite is now being largely utilized in various types of refractory blocks and several processes have been developed for its manufacture. The scope of the present investigation is confined to fire clay refractories, one of the aluminous type and the other of the siliceous type, in both of which we find mullite development after firing, and both of which are in general use as glass tank refractories.

The work may be summarized as follows:

(1) Two types of glass tank refractories were studied with respect to their chemical relationship with the molten glass, one aluminous and one siliceous.

(2) Calcination of the aluminous clay to cone 16 at the end of 60 hours failed to reveal any volatilization of alkalis and alkaline earths.

(3) Microscopic examinations were made on two samples, the aluminous clay burned to cone 28 and the siliceous clay burned to cone 23⁺. Indices of the aggregate and the glass were measured.

(4) A series of $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses were prepared and the refractive indices and the sp. gr. were determined.

(5) Mullite content was determined by (a) refractive indices and sp. gr. measurement and (b) hydrofluoric acid digestion. The aluminous clay burned to cone 28 contains 46% mullite. The siliceous clay burned to cone 23+ contains 14%.

(6) Mullite obtained from hydrofluoric acid digestion of the burned samples gives $n=1.67$ and $\gamma=1.70$. Chemical analysis gives 1.27% Fe_2O_3 and 3.16% TiO_2 .

(7) The physical properties of the glass matrix were studied. Relative viscosity was determined. The siliceous glass is more viscous than the aluminous glass at their respective fusion temperatures.

(8) Microscopic examinations were made on six samples of used tank blocks. The porcelainous layer adjacent to the refractory and the brown layer in the case of aluminous blocks or the milky white layer in the case of siliceous blocks were examined. Mullite and in some cases corundum and an aluminous glass were found in the porcelainous layer. A soda-lime feldspar was found in the brown layer in the case of aluminous blocks, while cristobalite was found crystallized out in the milky white layer in the case of siliceous blocks.

(9) Chemical analysis was made on the brown layer. It corresponds to a feldspar glass of the composition,



(10) The data were thoroughly discussed from the standpoint of thermochemical equilibrium.

REVIEW OF LITERATURE

The deterioration of tank blocks was clearly presented by Ross¹ in his paper with illustration of cases such as downward facing surfaces produced by shelving which in turn developed from horizontal joints or cracks and the thimble like gas blebs present in the upper extremities of the cavities above the upward drilling glass. Rosenhein² investigated the phenomena of pot attack by actually measuring the decrease in diameter of cylindrical clay bars immersed in molten glass. He gave two types of attack, one with a V taper on the rod and the other an A taper. The former takes place when the glass which takes clay into solution becomes lowered

¹ D. W. Ross, J. Am. Cer. Soc. 9, 641-653

² W. Rosenhein, J. Soc. Glass Tech. 3, 93-116

in density and it is displaced upward by the denser glass. But an increase in density in the resultant glass will produce an A taper on the rod. Hyslop³ carried on a similar experiment with respect to the density of the solute rich glass and the size of particles of the refractories. Flint and Payne⁴ dissolved in a glass (sp. gr. 2.46) 6% of Al_2O_3 in the form of clay and obtained a heavier glass (sp. gr. 2.50). The heavier glass sinks downward leaving fresh surface of the refractory for further attack, hence the upward solution. The difference in density will result in something like a convection flow. McCauley⁵ observed the existence of convection currents in glass tanks, though it may be due to convection of heat. Hess⁶ claims that unequal heating causes circulation of glass which has been contaminated by the refractory thus spoiling the melt.

It is also a known fact that the corrosion by glass itself is very much slower than that due to the batch constituents, especially the alkali salts. The experiments of Dr. Turner and his associates⁷⁻¹¹ show clearly that all alkali salts attack well burnt clays excessively even at as low a temperature as 800° C. Compared with carbonate and nitrate, Na_2SO_4 has only a slight action. A definite and notable increase in the degree of corrosion was observed in connection with the increase of salt cake. This, however, was explained as a result of reducing atmosphere and high temperature. Ross¹² claims that excessively reducing tank atmosphere accelerates the solution at the glass line, especially noticeable when excess salt cake is used in the batch. McSwiney¹³ claims that the shortening of tank life is independent of the amount of selenium used or the form in which it is used but varies with the amount of arsenic used in conjunction with the selenium. On the other hand Dr. Turner¹⁴ used an amount of As_2O_3 four or five times that used in practice and found no marked corrosion of fire clay as shown by the increase in the amount of Al_2O_3 and Fe_2O_3 taken into solution by the glass. Even though As_2O_3 is present in very small amount and cannot be shown to have any direct chemical reaction, it may play the role of a "mineralizer" in the formation of crystalline silicates in a molten

³ J. F. Hyslop, R. Gumm & H. Biggs, *J. Soc. Glass Tech.* 10, 405-424

⁴ F. C. Flint and A. R. Payne, *J. Am. Cer. Soc.* 9, 613-617

⁵ J. V. McCauley, *J. Am. Cer. Soc.* 8, 493-504

⁶ H. W. Hess, *Glass Worker*, 41, 11

⁷ D. Turner & W. E. S. Turner, *J. Soc. Glass Tech.* 7, 207-217

⁸ E. M. Firth, F. W. Hodkin, D. Turner & W. E. S. Turner, *J. Soc. Glass Tech.* 7, 218-227

⁹ E. M. Firth, F. W. Hodkin & W. E. S. Turner, *J. Soc. Glass Tech.* 7, 228-237

¹⁰ W. E. S. Turner, *J. Soc. Glass Tech.* 8, 284-285

¹¹ W. E. S. Turner, *J. Soc. Glass Tech.* 9, 28

¹² D. W. Ross, *J. Am. Cer. Soc.* 9, 641-653

¹³ D. W. McSwiney, *J. Am. Cer. Soc.* 8, 307-309

¹⁴ W. E. S. Turner, *J. Am. Cer. Soc.* 9, 412

magma¹⁵. The small amount of arsenic may alter materially the surface tension of the glass¹⁶ and may affect corrosion in the gaseous state. McCauley¹⁷ observes that the more resistant the clay, the deeper the holes ultimately become and the more pronounced they are. Diffusion of the gas in this connection is not an impossible explanation. Arthur and MacGee¹⁸ attempted to explain the upward drilling as essentially a solution of refractory by glass through the vapor phase which contains possibly the volatile alkalis.

Let us consider the corrosion phenomenon from the standpoint of chemistry. The ordinary glass is more or less saturated with silica, lime and soda and deficient in and quite unsaturated with alumina. It is clearly shown in the system $\text{SiO}_2\text{-Na}_2\text{OSiO}_2\text{-CaOSiO}_2$ ¹⁹ that the commercial soda lime glass has a composition very near to that of the ternary eutectic "O" (73.5% SiO_2 , 5.2% CaO). On the other hand, the refractory is saturated with respect to alumina and silica and quite unsaturated with respect to lime and soda. As a consequence, alumina, and to a smaller extent, silica, will be dissolved from the block into the glass. After a time the glass will be saturated with alumina in the zone immediately adjacent to the block and this combining with silica will crystallize out to form the white porcelain layer, consisting principally of mullite. Next to the porcelain layer, there is a layer of brown glass. This will fall principally into the feldspar family of silicates.

Dr. Sosman²⁰ considers the tank block corrosion theoretically from the standpoint of phase rule. The juxtaposition of a molten glass of the composition $\text{Na}_2\text{O CaO } 6\text{SiO}_2$ and the refractory of the composition $\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$ produces a system which is not in equilibrium. The alumina bearing crystalline phase, mullite, must therefore immediately begin to dissolve. Silica, as experience shows, also is dissolved from the refractory and the presumption is that this reaction, also, is one leading towards equilibrium. Phases which might possibly result from attainment of equilibrium at approximately 1350° C. within the system (glass-refractory) are corundum, mullite, tridymite, $\text{Na}_2\text{O } 2 \text{SiO}_2$, pseudo-wollastonite, series of soda-lime feldspars and aluminous liquid glass. In the four component system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O}$, not more than four of these phases could exist together and the aluminous glass

¹⁵ R. B. Sosman, J. Am. Cer. Soc. 8, 191-204

¹⁶ Glass and Refractories Symposium, Bull. Am. Cer. Soc. 5, 608

¹⁷ Glass and Refractories Symposium, Bull. Am. Cer. Soc. 5, 607

¹⁸ E. P. Arthur and A. E. MacGee, Glass Ind. 7, 107

¹⁹ Morey & Bowen, J. Soc. Glass Tech, 9, 226-262

²⁰ R. B. Sosman, J. Am. Cer. Soc. 8, 191-204

would almost certainly be one of the four. But what phases really exist in such a system? Wilson²¹ listed among the crystals formed by the action of glass on aluminous material "sillimanite,"* corundum, magnetite, biotite and feldspars. He found that the absorption rim between refractory and glass is composed of material which crystallized out as feldspars such as albite or soda leucite. Since this "sillimanite" is now being identified as mullite, the formation of corundum may be considered as a secondary product. The mullite was first formed and afterward decomposed into a liquid and corundum. Insley's work on stones²² in glass and the interface between refractory and glass²³ gives us some concrete information as to the mineralogical constitution. The narrow white porcelain zone so often seen at the interface between refractory and glass is composed of a net-work of mullite crystals in a matrix of glass. The glassy matrix of the white layer seems to dissolve readily in the molten soda-lime glass and the surface of the mullite crystal also shows traces of solution. Adjacent to the contact zone, there is very frequently a layer of corundum formed by the supersaturation of alumina in the contact zone and deposited simultaneously with the further solution of clay. Next to the zone of corundum and farther from the refractory is a zone of nephelite with considerable glass as inclusions. It is probable that nephelite crystallized out during cooling and the zone is rather infrequently observed. In his examination of thermocouple protection tubes that failed in glass melting furnaces, Insley²⁴ again observed the different layers. In this case, there is a vitreous zone between body and glaze consisting of short stubby prisms of mullite crystals and interstitial glass. In the next outer zone, there are small but well formed plates of corundum imbedded in glass. Then the vitreous outer zone contains glass and an artificial soda-lime feldspar with the optical properties of labradorite. In their work with commercial sillimanite, Couson and English²⁵ found by microscopic examination that there is a continuous transformation of unchanged sillimanite into mullite and this in turn gives up silica to yield, eventually corundum, which is found adjacent to the glass. The amount of corundum formed in the transformed layer is insufficient to form more than a widely spaced mesh, through which corrosive

²¹ G. V. Wilson, *J. Soc. Glass Tech.* 2, 177-216

* "Sillimanite" is equivalent to mullite but it is retained in the text to give the exact quotation of the original author.

²² H. Insley, *J. Am. Cer. Soc.* 6, 706-716; 7, 14-18

²³ H. Insley, *J. Am. Cer. Soc.* 7, 583-593

²⁴ H. Insley, *J. Am. Cer. Soc.* 8, 605-610

²⁵ A. Couson, S. English & W. E. S. Turner, *J. Soc. Glass Tech.* 9, 334-371

action on the sillimanite or mullite behind can continue. Barbordow²⁶ reports that as a result of the reaction between glass and fire clay, incrustation is formed which represents the composition of feldspar, a composition which though readily fusible is yet the most stable.

RAW MATERIALS USED IN THIS INVESTIGATION

In selecting a tank block refractory, a glass manufacturer always considers the advantages and disadvantages of using an aluminous block or a siliceous one, and the final choice of refractory by all manufacturers can never be the same, since many factors enter into the problem of glass tank corrosion and particular cases can never be controlled under a common rule.

Let us consider the question in general.²⁷ With an aluminous clay, the contact between glass and refractory is almost a straight line and one passes from the glass to the vitrified clay full of "sillimanite" needles and any absorption of the refractory material that takes place is gradual and complete. With the siliceous clay, however, the glass is in direct contact with the clay and can often be seen eating its way into and honeycombing it. The life of a refractory depends on the balance between the rate of formation and of solution of the white "sillimanite" layer. For an aluminous clay, the net-work of "sillimanite" needles acts as a protective layer. If the clay is siliceous, the "sillimanite" is dissolved as soon as it is formed. Consequently the refractory is rapidly eaten away by the molten glass which is constantly absorbing all the alumina available to form feldspar molecules in the glass. Bartsch²⁸ states that aluminous clays were less attacked since the protective layer of mullite and sometimes corundum formed more quickly than it could be dissolved away by the glass.

For the present investigation both aluminous and siliceous clays were included. The main object is to determine the amount of mullite developed in each clay and its relation to the equilibrium between glass and refractory.

For the aluminous clay, a dark refractory ball clay was employed (Mandle Porter No. 4 dark ball clay from Whitlock, Tennessee, supplied by Mr. D. W. Ross, Findlay Clay Products Company). The hygroscopic moisture content varies from day to day,

²⁶ M. A. Barbordow, *Keram. Rund.* 35, 515

²⁷ G. V. Wilson, *J. Soc. Glass Tech.* 2, 177-216

²⁸ O. Bartsch, *Glasstech. Ber.* 3, 249

the average being about 5%. The chemical analysis made on the dried sample is as follows:

	Dried Sample	Ignited Sample (calculated)
SiO ₂	45.55	53.01
Al ₂ O ₃	35.68	41.52
Fe ₂ O ₃	1.16	1.35
TiO ₂	2.81	3.27
CaO	0.11	0.13
MgO	0.11	0.13
K ₂ O	0.14	0.16
Na ₂ O	0.37	0.43
Ignition loss	13.75	
	99.68	100.00

If we consider only SiO₂ and Al₂O₃, we have 56.08% SiO₂ and 43.92% Al₂O₃ or a composition with the molecular formula Al₂O₃: 2.17 SiO₂.

The softening temperature is cone 33⁺

The clay is ground to pass 100 mesh sieve and treated with a magnet.

The siliceous clay is prepared by blending the aluminous clay with flint in the following proportions:

40% by weight aluminous clay
60% by weight ground flint

The flint used is a sample from National Silica Company. The chemical composition is as follows:

SiO ₂	99.752	
Al ₂ O ₃	0.032	
Fe ₂ O ₃	0.026	(Analyzed by D. J. Demorest)
TiO ₂	0.008	
CaO	0.020	
MgO	0.017	
K ₂ O	0.017	
Na ₂ O	0.022	
Ignition loss	0.106	

This is sieved through 100 mesh screen and treated with a magnet before the blending.

The blended siliceous clay has the following compositions: (calculated)

	Dried Sample	Ignited Sample
SiO ₂	78.07	82.79
Al ₂ O ₃	14.29	15.15
Fe ₂ O ₃	0.48	0.51
TiO ₂	1.13	1.20
CaO	0.06	0.06
MgO	0.05	0.05
K ₂ O	0.07	0.07
Na ₂ O	0.16	0.16
Ignition loss	5.56	
	99.87	100.00

Considering SiO₂ and Al₂O₃ alone we have 84.51% SiO₂ and 15.49% Al₂O₃, which corresponds to the molecular formula Al₂O₃: 9.275 SiO₂.

The softening temperature is cone 27.

EXPERIMENTAL RESULTS WITH MATERIALS USED

PHYSICAL PROPERTIES OF THE BURNED CLAYS

Bars were made from both clays and burned to cone 11+ in a commercial kiln. Their physical properties are as follows:

	Sp. gr.	Absorption	Modulus of Rupture
Aluminous grog	2.744	0.08%	5660 lbs. per sq. in.
Siliceous grog	2.576	15.2%	2870 lbs. per sq. in.

The bars were crushed to about 3 mesh and used as grogs in the next burn.

With 50% of the grog prepared and 50% raw clay, bars were made from both clays and burned to cone 12+ in a commercial kiln. They have the following properties:

	Sp. gr.	Absorption	Modulus of Rupture
Aluminous body	2.745	10.4%	3980 lbs. per sq. in.
Siliceous body	2.526	20.5%	1240 lbs. per sq. in.

CALCINATION OF ALUMINOUS CLAY

While the burning was carried on in the commercial kiln, a separate burn was made at the laboratory with the idea of ascertaining the possible volatilization of alkalies and alkaline earths during the heat treatment. Cones were made from the aluminous clay and

burned in a small gas fired furnace. The firing schedule is as follows:

Total heating time	60 hours
Up to cone 12	50 hours
Cone 12 to cone 14	3 hours
Cone 14 to cone 16	7 hours

The burned cones have a sp. gr. of 2.724 and an absorption 0.08%.

The cones were broken off from the plaque and the tips were ground to a fine powder. Two chemical analyses were made on this sample of ground cone tips.

	I	II
SiO ₂	52.58	52.68
Al ₂ O ₃	41.21	41.26
Fe ₂ O ₃	1.31	1.30
TiO ₂	3.24	3.21
CaO	0.13	0.12
MgO	0.14	0.13
K ₂ O	0.16	0.17
Na ₂ O	0.42	0.47
Ignition loss	0.20	0.20

If we take the average of the two and calculate to 100% basis minus the ignition loss and compare with that of the raw clay minus its ignition loss, then we have:

	Cone Tips	Ignited Raw Clay
SiO ₂	53.02	53.01
Al ₂ O ₃	41.53	41.52
Fe ₂ O ₃	1.32	1.35
TiO ₂	3.25	3.27
CaO	0.13	0.13
MgO	0.13	0.13
K ₂ O	0.17	0.16
Na ₂ O	0.45	0.43

There is practically no change in the chemical composition even after burning for 60 hours. Since the cones are small, the heat treatment will not be widely different from the actual conditions in commercial kilns. The data indicate in this clay at least, that the alkalis were probably present as feldspars or other silicates and even a long heat treatment would not cause their volatilization.

MICROSCOPIC EXAMINATION

The various samples were studied with the aid of a petrographic microscope. In all cases, however, the crystals developed during the burning are so small that they cannot be examined without the aid of an oil immersion objective. Again the only optical properties worth studying is the refractive index. When the grains possess some definite shape, the sign of elongation is also determinable. But for most cases, the average index of the aggregate is measured with a low power objective. In some cases, glass is found detached from the aggregate and its index is accordingly determined. Here again if there are some very minute crystals imbedded in the glass, a higher index will be obtained. As the average index of the aggregate means the average between the crystal and the glass in proportion to their volume percentages, an approximate percentage of crystal in the aggregate can be calculated if we can determine the indices and the sp. gr. of the crystal and of the glassy phase.

The following data was obtained from various samples but they are of little value because neither the crystal nor the glass can be examined independently.

(a) Cone tips (cone 16)

Index of aggregate	1.58
Index of glass	1.508
Crystal phase undeterminable.	

(b) Aluminous grog (cone 11+)

Index of aggregate	1.565
Index of glass	1.510
Crystals are very minute with an average index 1.67.	

(c) Siliceous grog (cone 11+)

Index of aggregate	1.53
Index of glass	1.505
Considerable residual mineral is present as quartz and some inverted to cristobalite.	

(d) Aluminous body with 50% grog (cone 12+)

Index of aggregate	1.56
Index of glass	1.510
Crystals are very minute. Average index = 1.68	

(e) Siliceous body with 50% grog (cone 12+)

Index of aggregate	1.53
Index of glass	1.505
Considerable quartz and some cristobalite are present.	

The result is somewhat discouraging since the crystals developed in all cases are too small for the determination of their optical

properties. With the siliceous grog, it is evident that quartz is a residual mineral and some has inverted to cristobalite. It is therefore decided to prepare a body with 50% grog and burn it near its deformation temperature, anticipating that the crystals may develop to a larger size and in the case of siliceous body the reaction between quartz and clay may be carried a little further.

PREPARATION OF A BODY WITH 50% GROG TO BE FIRED NEAR THE DEFORMATION TEMPERATURE

The grog was ground to pass 100 mesh and treated with a magnet. A batch was made up with 50% grog and 50% raw clay and thoroughly mixed. With the addition of water, "spaghetti" was made from the batch by squeezing it through a small nozzle. It has

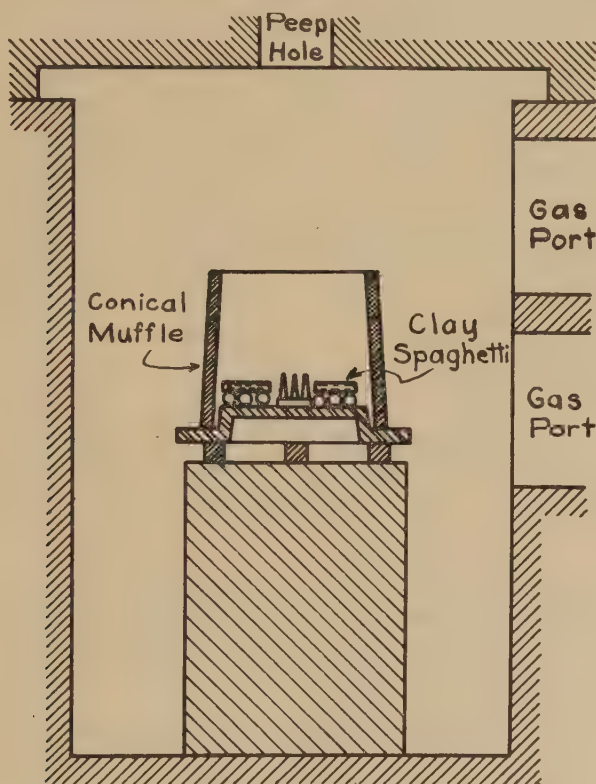


FIG. 1. GAS FIRED MEKER FURNACE FOR BURNING THE SPAGHETTI.

a diameter of about $1/16$ of an inch. This spaghetti was then baked in a small electric furnace to give it enough strength to be handled. It was then broken into pieces about one inch in length. These were laid in two layers and burned in a gas-fired Meker furnace (Fig. 1.)

The temperature is controlled with an optical pyrometer and standard cones. The spaghetti of the bottom layer was discarded because of its contact with the plaque. After some experiment, it was decided to burn the two bodies to different temperatures in order to produce a fair amount of crystal development and at the same time to keep them below their respective softening temperatures. The aluminous spaghetti was heated up to cone 28, held for two hours and cooled in air. The siliceous spaghetti was heated up to come 23+, held for two hours and cooled in air. The spaghetti was then powdered for microscopic examination.

The sp. gr. determination gives—

Aluminous spaghetti	2.782
Siliceous spaghetti	2.428

MICROSCOPIC EXAMINATION OF BURNED SPAGHETTI

Measurements were made on the refractive indices of the aggregate and of the glass with the petrographic microscope.

(a) Aluminous Spaghetti

Index of aggregate.....	1.58
Index of glass.....	1.505

Considerable crystals are developed in patches imbedded in glass but clean grains are very scarce. Some of the grains give an index between 1.68 and 1.69.

(b) Siliceous Spaghetti

Index of aggregate.....	1.50
Index of glass.....	1.480

Some isotropic cristobalite of an index 1.485 is observed alongside with unaltered quartz but it is rather difficult to distinguish the cristobalite from the glass whose index is 1.48. In some cases, however, the cristobalite shows a slight birefringence.

PREPARATION OF Al_2O_3 - SiO_2 GLASSES

From the microscopic examination, we obtain the indices of the glass phase. But the primary object of this investigation was to determine the percentage of mullite and glass developed in the clay when burned to a certain temperature. In order to accomplish this we have to know the chemical composition and the physical properties of the glass phase. Kraner²⁹ has made several glasses with corundum and flint by melting the mixture in an oxy.-gas flame. His data are too scanty for our purpose. Bowen and Greig³⁰ also have some data on glasses near to the silica end. Their results are shown together with the data obtained by the author in Fig. 3.

²⁹ H. M. Kraner, J. Am. Cer. Soc. 8, 726-34

³⁰ Private communication from Dr. N. L. Bowen.

For the present purpose, instead of using chemically pure Al_2O_3 and SiO_2 , it was decided to use the aluminous clay and flint employed since the beginning of this investigation, because the resulting glass will contain approximately equal amount of impurities as found in the glass matrix developed on heating the clay, assuming, of course, that the impurities (RO's) will distribute themselves proportionately between the mullite crystal and the glass. This assumption is allowable since the deviation resulting from such an assumption is far below the accuracy anticipated in this investigation.

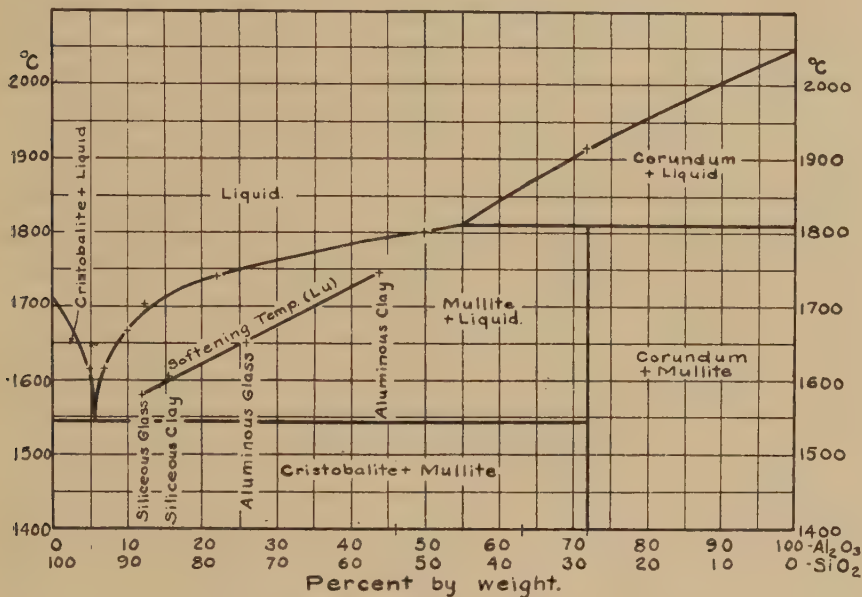


FIG. 2. SYSTEM Al_2O_3 - SiO_2 (BOWEN AND GREIG).

Ten glasses were then prepared with their compositions varying from the mullite- SiO_2 eutectic point to the clay composition. The mixtures were made into fine spaghetti exactly like the clay ones and baked just strong enough to be handled. Instead of burning in a furnace, the spaghetti was burned in a gas-oxygen flame and the molten glass was chilled in water. The clear portion of the glass beads was then picked out, ground to a fine powder and treated with a magnet. Determination of sp.gr. and refractive index was made on this sample.

Glass No.	% Al_2O_3 by weight	Sp.gr. (25°C.)	N_D
AS 1	5.53	2.219	1.470
AS 2	6.53	2.234	1.472

AS 3	8.50	2.253	1.475
AS 4	11.01	2.278	1.478
AS 5	14.99	2.313	1.484
AS 6	19.96	2.363	1.493
AS 7	24.96	2.419	1.502
AS 8	29.93	2.445	1.514
AS 9	34.89	2.471	1.526
AS 10	39.54	2.519	1.537
Aluminous clay	43.92	2.566	1.549
Siliceous clay	15.49	2.319	1.486

The indices are shown in Fig. 3. From the data of Bowen and Greig the index of the glass is a linear function of the composition. Of course they used chemically pure Al_2O_3 and SiO_2 . In the present case, the clay employed contains about 4.5% Fe_2O_3 and TiO_2 which find their way into the glass phase and thus raise the refractive index. This is clearly shown by the greater deviation of the author's curve from Bowen's at the clay end where more Fe_2O_3 and TiO_2 enter into the glass composition. Judging from the "smoothness" of the curve it can be safely said that by measuring the refractive index of a glass, we can locate approximately its composition between the eutectic and clay point.

Sp. gr. determinations were also made on these glasses. The pycnometer method was used. The thermostat was kept constant at 25°C. The sp. gr. of the glass is practically a linear function of the composition as shown in Fig. 4.

From Figs. 3 and 4 we obtain graphically.

	Index	% Al_2O_3	Sp. gr.
Aluminous glass	1.505	26.2	2.41
Siliceous glass	1.480	12.0	2.29

SEPARATION OF MULLITE

Navies³¹ determined the quantity of mullite developed in fire clay by X-ray method and showed that a ball clay or china clay can develop the maximum quantity of mullite theoretically possible. Rees³² determined the mullite content by digesting 1 gram of sample with 20 cc pure hydrofluoric acid at 20°C. for 12 hours. The proportion of mullite present in the fire clay increases with alumina content of the clay and with the temperature and duration of the heat treatment. Thompson and Vermelker³³ used the same method

³¹ N. Naviss, J. Am. Cer. Soc. 8, 296-302

³² W. J. Rees, Trans. Cer. Soc. 24, 23

³³ F. S. Thompson and R. I. Vormelker, J. Am. Cer. Soc. 9, 639-640

but their results do not justify any definite conclusion. McVay³⁴ tried digestion with hydrofluoric, sulphuric and phosphoric acids but no definite conclusion is reached.

After some experiments it was decided to use hydrofluoric acid to digest the glass matrix. In order to reduce the effect of HF on mulite crystals 20 cc of a 15% HF solution together with 3 drops of

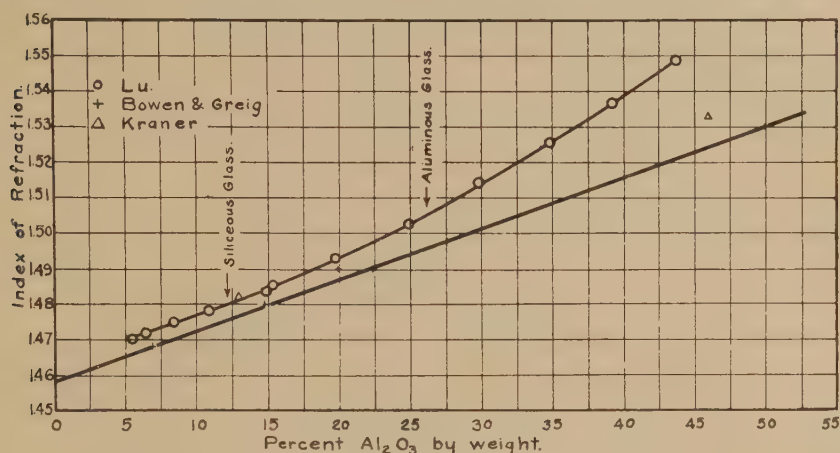


FIG. 3. INDICES OF REFRACTION OF Al_2O_3 - SiO_2 GLASSES.

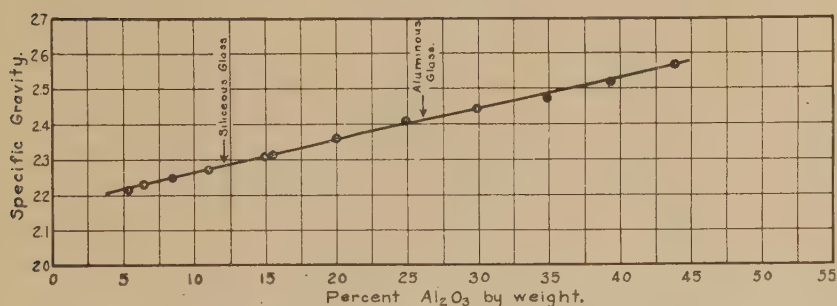


FIG. 4. SPECIFIC GRAVITY OF Al_2O_3 - SiO_2 GLASSES.

concentrated H_2SO_4 was employed to digest a sample of about 0.5 gram. This was done in a platinum crucible and washing was done by addition of water and repeated decantation. In some cases, this was followed by another washing with dilute HCl and subsequent washings with water. The residue was filtered, dried and ignited very gently just to burn off the filter paper. The difference in weight before and after the treatment is taken as the percentage of glass present and the residue is considered the percentage of the crystal. This is confirmed by microscopic examination. If the crystal left appears impure under the microscope, i. e., still attached to the

³⁴ T. N. McVay, J. Am. Cer. Soc. 10, 62

glass matrix, subsequent digestion and washings are followed. When the crystal appears clean, all its optical properties determinable are carefully measured.

The digestion data on the aluminous spaghetti and the siliceous spaghetti are as follows:

(A) Aluminous Spaghetti (cone 28)

1. Treated with 20 cc 15% HF and 3 drops of H_2SO_4 , kept over water bath ($75\text{--}80^\circ\text{C}.$) for three hours and followed by subsequent washings.

Amount of residue=53.1%

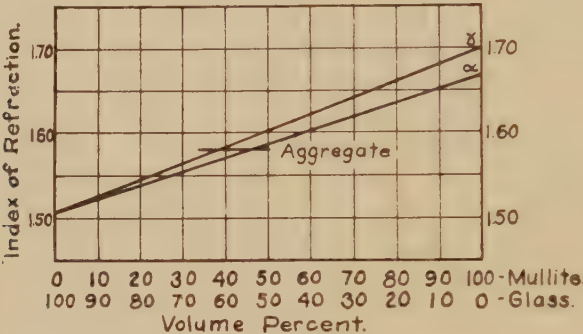


FIG. 5a. MULLITE CONTENT IN ALUMINOUS CLAY.

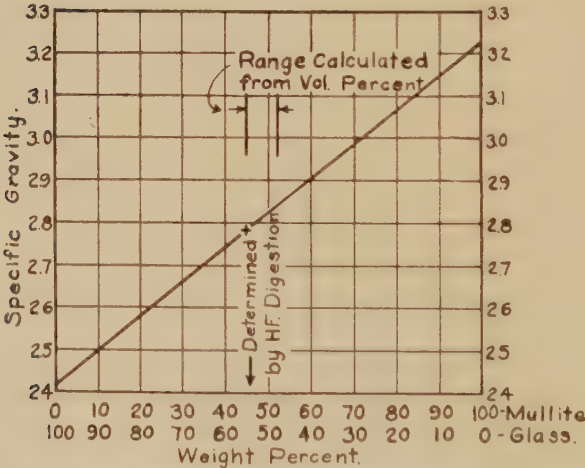


FIG. 5b. MULLITE CONTENT OF ALUMINOUS CLAY AS DETERMINED BY DIFFERENT METHODS.

Some glass is still visible with minute crystals imbedded in them. The average index of this glass is 1.54 to 1.55. The crystal has an index 1.68.

2. Treated with 20 cc 15% HF and 3 drops of H_2SO_4 , kept standing at room temperature (about $20^\circ\text{C}.$) for 24 hours and followed by subsequent washings.

Amount of residue=54.2%

The crystal has an index 1.68. Some glass is still present. The sample is then treated with dilute HCl and followed by subsequent washings. The residue is filtered, dried and gently ignited.

Amount of residue=45.7%

The crystals in the residue are quite clean. The indices were measured. $\alpha = 1.67$. $\gamma = 1.70$. Biaxial and positive. Parallel extinction and positive elongation. This is a very good sample of mullite.

3. Treated with 20 cc 15% HF and 3 drops of H_2SO_4 , kept standing at room temperature for 36 hours and followed by subsequent washings.

Amount of residue=50.2%

The residue is treated with dilute HCl and followed by subsequent washings. Filtered and gently ignited.

Amount of residue=45.1%

Practically there is no difference from the previous digestion even though time is lengthened to 36 hours. Crystals are fairly clean. The indices are 1.67 and 1.70.

4. Same treatment as digestion No. 2.

Amount of residue=47.2%

Indices of crystals are 1.67 and 1.70.

5. Treated with 20 cc 15% HF and 3 drops of H_2SO_4 , kept standing at room temperature for 3 hours and followed by subsequent washings.

Amount of residue=68.0%

Considerable glass is left. Index of glass is 1.505. Crystals have an average index 1.68 but not clean enough for good measurements.

It is thus clearly shown that the digestion process is fairly under way in the first three hours and the digestion velocity is gradually decreasing until the complete solution of the glass. Together with the volatilization of SiF_4 and consequent dilution of the existing acid, the strength of the solvent is falling off rapidly and its effect on the crystal can be practically neglected. But in order to show the other extreme case, the following digestion is made.

6. Treated with 20 cc 15% HF and 3 drops of H_2SO_4 , kept over water bath for 3 hours and finished with boiling and subsequent washings.

Amount of residue=19.7%

The indices of the crystals are 1.67 and 1.70. The sample is considerably contaminated with decomposition product. There is practically no trace of glass matrix.

From the data thus obtained, it is concluded that the digestion with 15% HF and a few drops of concentrated H_2SO_4 at room temperature for 24 hours or over water bath for 3 hours, followed by washings with dilute HCl and water, gave closely reproducible results and the crystals so obtained were fairly clean for micro-

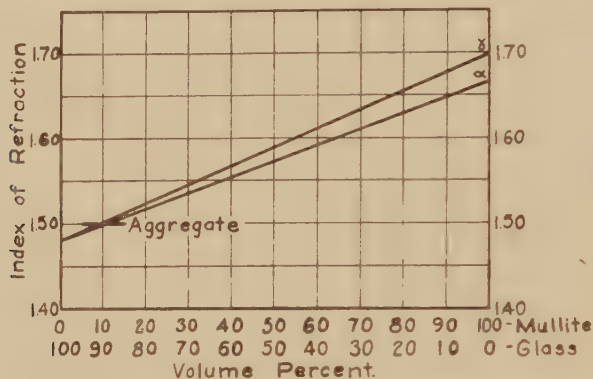


FIG. 6a. MULLITE CONTENT IN SILICEOUS CLAY.

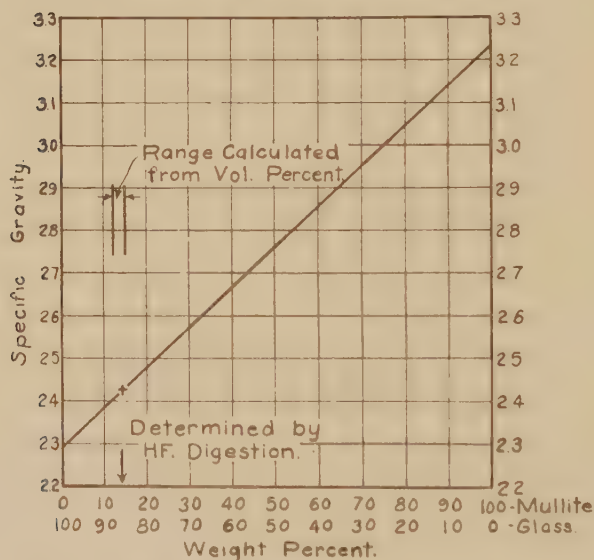


FIG. 6b. MULLITE CONTENT OF SILICEOUS CLAY AS DETERMINED BY DIFFERENT METHODS.

scopic determination. If we take the values from digestions Nos. 2, 3 and 4 we have 45.7%, 45.1% and 47.2%. The average is 46% mullite in the aluminous spaghetti when burned to cone 28.

(B) Siliceous spaghetti (cone 23+)

From the experience gained in digesting the aluminous spaghetti with HF and H₂SO₄, the siliceous spaghetti was treated exactly in the same manner. The digestion data is as follows:

1. Treated with 20 cc 15% HF and 3 drops of H₂SO₄, kept over water bath for 3 hours and followed by washings.

Amount of residue=15.4%

Crystals are not very clean. The average index is 1.68.

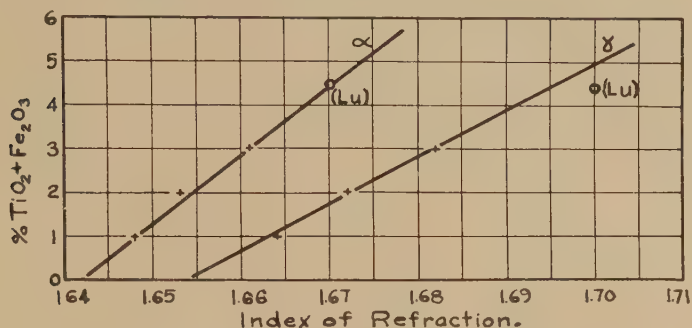


FIG. 7. INDICES OF MULLITE (BOWEN AND GREIG).

2. Similar to No. 1, followed by washings with dilute HCl and water.

Amount of residue=14.1%

Indices of crystal are 1.67 and 1.70. There is practically no glass left.

3. Similar to No. 2.

Amount of residue=13.8%

Indices of crystals are 1.67 and 1.70.

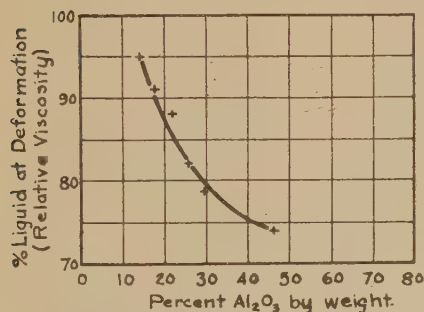


FIG. 8. VISCOSITY OF Al₂O₃-SiO₂ GLASSES (GOULD).

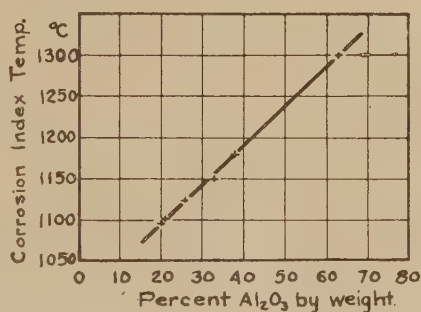


FIG. 9. CORROSION INDEX (HYSLOP).

4. Treated with 20 cc 15% HF and 3 drops of H₂SO₄, kept standing at room temperature for 24 hours and followed by washings with dilute HCl and water.

Amount of residue=14.1%

5. Treated with 20 cc 15% HF and 3 drops of H₂SO₄, kept standing over water bath for 3 hours and followed by boiling and subsequent washings.

Amount of residue=5.9%

Indices of crystals are 1.67 and 1.70. The samples are greatly contaminated with decomposition product.

With practically the same treatment used with the aluminous spaghetti we get from digestions Nos. 2, 3, and 4; 14.1%, 13.8% and 14.1% respectively. The average is 14% mullite in the siliceous spaghetti when burned to cone 23⁺.

The mullite crystals thus obtained from different samples vary a little in indices but all lie between 1.67 and 1.70. Some very clean crystals give $\alpha = 1.668$ and $\gamma = 1.698$. The sp. gr. of the mullite separated is 3.23 (25°C.). The chemical analysis is as follows:

SiO ₂	24.12
Al ₂ O ₃	70.74
Fe ₂ O ₃	1.27
TiO ₂	3.16
CaO	0.07
MgO	0.06
	99.42

By extrapolating from Bowen's value³⁵ of indices of mullite (Fig. 7) we have for mullite containing 4.4% TiO₂ and Fe₂O₃, $\alpha = 1.670$ and $\gamma = 1.695$, while our values are $\alpha = 1.67$ and $\gamma = 1.70$.

CORRELATION OF DATA

(A) Aluminous spaghetti (cone 28)

	Index of refraction	Sp. gr.
Aggregate	1.58	2.782
Mullite	1.67-1.70	3.23
Glass	1.505	2.41 (from Fig. 4)

The refractive index of the aggregate is the average index between mullite and glass in proportion to their respective volume percentages. By plotting the indices against volume percentage we get the volume percentage of mullite and glass in the aggregate. Using the two indices of mullite, we get a range rather than a point on the diagram as shown in Fig. 5a from 38% to 45% of mullite by volume.

Now, we also know the sp. gr. of mullite and glass. By a simple calculation we get the weight percentage of mullite in the aggre-

³⁵ Bowen and Greig, J. Am. Cer. Soc. 7, 252

gate. Take, for instance, the lower value 38% of mullite by volume, we have then,

$$\begin{array}{rcl} \text{for mullite} & \dots\dots\dots & 38 \times 3.23 = 122.74 \\ \text{for glass} & \dots\dots\dots & 62 \times 2.41 = 149.42 \\ & & 122.74 + 149.42 = 272.16 \\ \\ \frac{122.74}{272.16} \times 100 & = & 45.1\% \text{ mullite by weight} \\ \frac{149.42}{272.16} \times 100 & = & 54.9\% \text{ glass by weight} \end{array}$$

Similarly for the higher value 45% mullite by volume we get 52.3% mullite and 47.7% glass by weight.

This is shown in Fig. 5b by two vertical lines indicating the range of mullite present in the aggregate in weight percent.

From the HF digestion data we have 46% mullite. This is indicated by an arrow in Fig. 5b. Again if we plot the sp. gr. of mullite and glass against weight percentage and locate the sp. gr. of the aggregate on the straight line joining the two, the amount of mullite in the aggregate can be approximately estimated. This is shown by a cross on the straight line in Fig. 5b. It gives 45% mullite by weight. Hence, we have,

- (1) By refractive index..... 45.1-52.3% mullite
- (2) By HF digestion..... 46% mullite
- (3) By sp. gr..... 45% mullite

Of course, the sp. gr. determination cannot be considered as a method for measuring the mullite content, because any corundum present will also increase the sp. gr. of the aggregate.

(B) Siliceous Spaghetti (cone 23+)

	Index of refraction	Sp. gr.
Aggregate	1.50	2.428
Mullite	1.67-1.70	3.23
Glass	1.480	2.29 (from Fig. 4)

Following the same process of calculation we have in the siliceous spaghetti burned to cone 23+.

- (1) By refractive index 9-10 % mullite by volume
Corresponding to 12.2-14.8% mullite by weight
- (2) By HF digestion 14 % mullite by weight
- (3) By sp. gr. 14.5% mullite by weight

PHYSICAL PROPERTIES OF THE GLASS MATRIX

From the determination of refractive index, we have:

	Index of Refraction	%Al ₂ O ₃ (from Fig. 3)	Sp. gr. (from Fig.)
Aluminous glass	1.505	26.2	2.41
Siliceous glass	1.480	12.0	2.29

In order to study these glasses more thoroughly, batches were made from flint and aluminous clay. Softening temperatures were determined with cone fusion.

	%Al ₂ O ₃	Softening temperature
Aluminous glass	26.21	Cone 30
Siliceous glass	12.02	Cone 23

If we plot these softening temperatures against composition together with the softening temperatures of the two clays employed we have as shown in Fig. 2 a softening temperature curve which is practically a straight line. It represents in a way the probable liquidus curve of mullite in the system "aluminous clay-flint." The presence of impurities must be recognized as important factors in the values obtained.

The next physical property to be measured is the relative viscosity of the glasses. Bowen³⁶ pointed out that the viscosity of the Al₂O₃-SiO₂ glass may not be a linear change with respect to composition but there is a general increase in the viscosity going over toward silica and a decrease in going over to alumina. Gould³⁷ measured the viscosity by the amount of liquid present at the deformation temperature. The more glass required for the same degree of deformation, the more viscous the glass is considered. The siliceous glass is more viscous than the aluminous one as shown in Fig. 8. Hyslop³⁸ made clay-glass mixtures into cones and measured their squatting temperature. This is designated as corrosion index temperature (Fig. 9.) It means the temperature at which the clay-glass mixtures have equal viscosities and the mullite content of the burned clay is the determining factor. If the fired clay contains any considerable amount of mullite, it will tend to form with the glass an intermediate layer of high viscosity.

Of course the viscosity of glass is a function of the temperature. The higher the temperature, the lower the viscosity. In order to measure the relative viscosity of the two glasses, spaghetti was made from both batches. Since the two glasses do not fuse at the same temperature, a comparison of viscosity at the same temperature seems meaningless. In this sense, Hyslop's corrosion index temperature is by no means a measure of viscosity but an indication of the increasing rigidity acquired by the glass-clay mixture as the clay content is increased. Hence to get a fair idea of the relative viscosity of these glasses as it is applied in studying the properties

³⁶ N. L. Bowen, Bull. Am. Cer. Soc. 3, 387

³⁷ R. E. Gould, Ohio State Univ., B. Cer. E. Thesis (1925)

³⁸ J. F. Hyslop, J. Soc. Class Tech. 10, 148

of glass tank refractories, it was decided to compare the relative viscosity at their respective fusion temperatures.

The spaghetti was first melted with a gas-oxygen flame into a bead and the bead was cooled on an asbestos board. The diameter of the beads was measured with a micrometer and pairs were matched by selecting one from each glass that has approximately the same diameter. Then the bead was held between the tips of a pincette which are covered with platinum foil. No extra force was exerted on the bead. It was then placed in the gas-oxygen flame again. After a lapse of three or four seconds, a bright glow is seen, the time is observed. When the glass becomes sufficiently fluid, it drops off by its own weight. The time is again observed. This interval of time observed in seconds is taken as a measure of the relative viscosity. The author recognizes that this is not strictly a measure of viscosity. It involves time and heat conductivity and perhaps many other factors, but it gives us a fair vision of the relative fluidity, if not viscosity, of the two glasses.

The bead never reaches the temperature of the flame which is observed with an optical pyrometer as high as 3200°F. or 1760°C. It drops off by its weight as soon as it develops enough liquid to cause it to lose its rigidity. The three or four seconds before the bright glow were allowed for the difference in heat conductivity of the two glasses.

For ten pairs of beads, we have—

	Aluminous glass	Siliceous glass
1	30 sec.	55 sec.
2	14	30
3	15	35
4	28	60
5	15	30
6	20	35
7	10	15
8	25	45
9	25	80
10	15	35
Total	197	420
Average	20	42

The aluminous glass is about twice as fluid or half as viscous as the siliceous glass at their respective fusion temperatures.

MICROSCOPIC EXAMINATION OF TANK BLOCKS

The microscopic examination was concentrated on the interface between the glass and the refractory. Starting from the refractory side, first there is the unaltered block, which is practically in the same condition as before it was put into service. There may be some growth of mullite during its service but this is of secondary importance in the present investigation. The next layer is white and porcelainous.. Then comes a layer of brown glass, supposed to be aluminous in composition, in contact with the tank glass.

Uneno ³⁹ analyzed several layers at the interface and examined them microscopically. The white layer consists of "sillimanite" crystals imbedded in glass together with quartz and tridymite. The brown layer consists entirely of glass. Wilson ⁴⁰ calculated the composition of this brown glass by subtracting "sillimanite" molecule from the clay composition and arrived at a formula $\text{Na}_2\text{O} : 1.41 \text{ Al}_2\text{O}_3 : 4.15 \text{ SiO}_2$. There is appreciable excess of alumina over soda leucite but the refractive index does not indicate any presence of corundum or any high aluminous glass. But if we recalculate his data on mullite basis, we shall have the glass composition higher in silica and lower in alumina, bringing the composition nearer to that of soda feldspar.

Insley ⁴¹ observed on the surface of an aluminous refractory in a glass furnace regenerator, deposits composed principally of nephe-lite, carnegieite and corundum. The first two can form probably only in those parts of the glass furnace where the temperature is considerably lower than that required to melt the glass but corun-dum may be formed at melting temperatures. McDowell ⁴² studied the interface between slag and boiler furnace fire clay refractory. The microscopic examination reveals that the outer coating consists of a plagioclase feldspar with a composition between bytown-ite and anorthite. As the body of the refractory is approached, mullite becomes the predominant crystalline phase. Peck ⁴³ observed in his study on microstructure of porcelain that "silli-manite" crystals develop (a) by a slow and gradual passage from the amorphous to the crystalline state without the aid of a flux and (b) with the aid of feldspar as a flux they form in well developed crystals in the feldspar glass at kiln temperatures, through the solution and recrystallization of amorphous "sillimanite." Scholes⁴⁴

³⁹ Z. Uneno, Asahi Glass Co. Rept. (Japan) 10, 67 (1923)

⁴⁰ G. V. Wilson, J. Soc. Glass Tech. 2, 177-216

⁴¹ H. Insley, J. Am. Cer. Soc. 9, 635-638

⁴² S. J. McDowell and H. C. Lee, J. Am. Cer. Soc. 11, 35-41

⁴³ A. B. Peck, J. Am. Cer. Soc. 2, 175-194

⁴⁴ S. R. Scholes, J. Am. Cer. Soc. 3, 498

applied a lining of feldspar-clay mixture to a pot melting lead-potash glass and obtained a vitreous coating which gave satisfactory results. Morozewicz⁴⁵ claims that melts having the composition of plagioclase feldspar are capable of dissolving excess of alumina which on cooling crystallizes out as corundum while excess of SiO_2 and Al_2O_3 in an albite melt separates out as "sillimanite" and corundum.

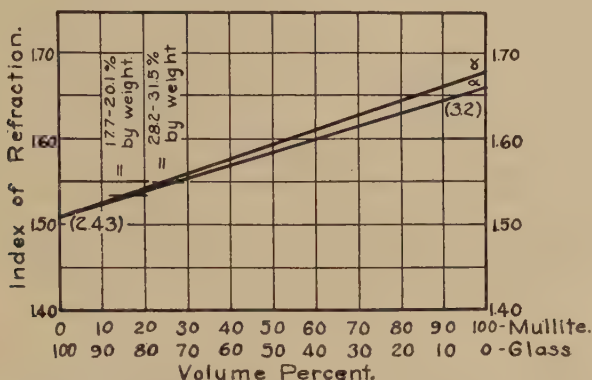


FIG. 10. PER CENT MULLITE DEVELOPED IN ALUMINOUS BLOCK.

For the present study six used blocks were selected. The different layers were separated as far as possible and each layer was ground to a fine powder for microscopic examination. Thin sections were also made showing the contact between the glass and the refractory.

(A) A used block from Federal Glass Company.

(1) White layer.

Crystals of mullite and some corundum were identified in this layer together with an aluminous glass which has an index 1.510. The β corundum has one index ($n=1.675$) very close to that of mullite and if the grain is too small, it is impossible to obtain any interference figure in order to distinguish it from mullite.

The aggregate has an average index of 1.55.

Assuming that the aggregate is composed mainly of mullite and glass matrix and applying the calculation of mullite content by

⁴⁵ J. Morozewicz, Tscherma Min. Pet. Mitt. 18, 56-57



FIG. 11a.



FIG. 11b.

FIG. 11a. SECTION SHOWING INTERFACE OF SAMPLE A. NOTE THE PARALLEL DEPOSIT OF LABRADORITE CRYSTALS AND THE PATCHES OF MULLITE DEVELOPED IN THE REFRACTORY. $\times 60$ DIAMETERS.

FIG. 11b. SAME AS FIG. 11a. CROSSED NICOLS



FIG. 11c.

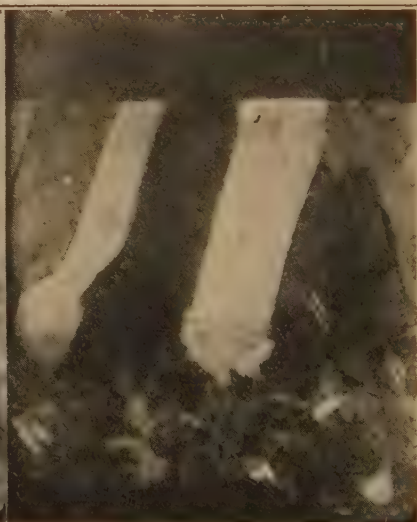


FIG. 11d.

FIG. 11c. LABRADORITE CRYSTALS SHOWN IN THE UPPER RIGHT HAND CORNER OF FIG. 11b. $\times 250$ DIAMETERS.

FIG. 11d. SAME AS FIG. 11c. CROSSED NICOLS.

using the indices and sp. gr. of the mullite and the glass, we have 23-26% by volume or 28.2-31.5% mullite by weight (Fig. 10). Of course this is only approximately true since there is some corundum present which also raises the index of the aggregate.

(2) Brown layer.

Index of glass is 1.512.

Crystals of mullite were found but scarce.

Another crystal was observed.

$$\alpha = 1.558$$

$$\gamma = 1.567$$

Biaxial and positive.

Two cleavages were observed, the extinction angle on one is 8° and on the other is 20° .

This is identified as labradorite with an approximate composition Ab_2An_3 ⁴⁶ i. e., 40 mol.% albite and 60 mol.% anorthite.

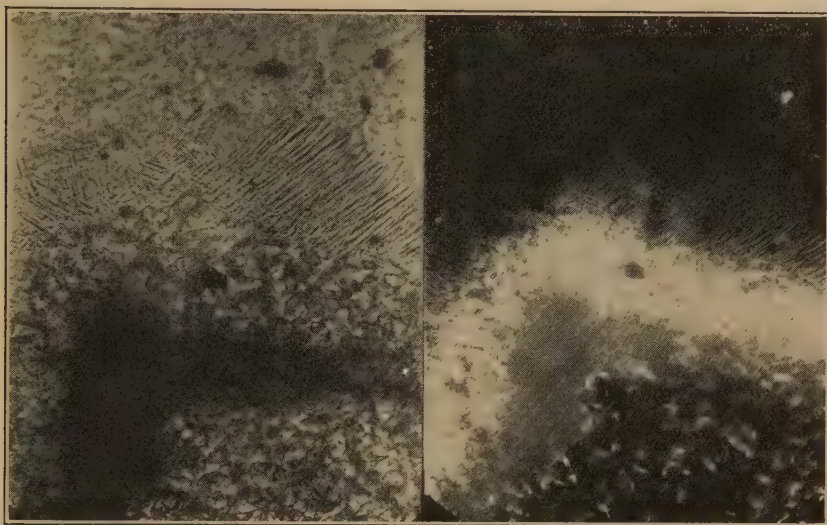


FIG. 12a.

FIG. 12b.

FIG. 12a. SECTION SHOWING INTERFACE OF SAMPLE B. NOTE THE WELL DEVELOPED CRYSTALS OF MULLITE AND THE FELDSPAR CRYSTALS BETWEEN THE MULLITE AND THE TANK GLASS. $\times 250$ DIAMETERS.

FIG. 12b. SAME AS FIG. 12a. CROSSED NICOLS.

Also some residual quartz and cristobalite were found but very scarce.

(3) Tank glass.

Index of tank glass is 1.508.

A photomicrograph of a section perpendicular to the interface is shown in Figs. 11a, 11b, 11c, 11d. Note particularly the manner

⁴⁶ A. N. Winchell, *El of Optical Mineralogy*, Pt. II, 279

in which the feldspar is deposited and the straight demarcation between the feldspar and the tank glass.

(B) A close-structured block that gave fair service, supposed to be more or less aluminous (supplied by Mr. Ross).

(1) White layer.

Mullite and corundum were identified together with an aluminous glass (index=1.508). The aggregate has an average index 1.535. With the same assumption and applying the same calculation, we have, 14-16% by volume or 17.7-20.1% mullite by weight (Fig. 10).

(2) Brown layer.

Mullite and labradorite were identified together with a feldspar glass (index=1.510).

(3) Tank glass.

No tank glass was available but it is said to be a commercial soda-lime glass for making bottles.

A photomicrograph of the interface is shown in Figs. 12a and 12b.

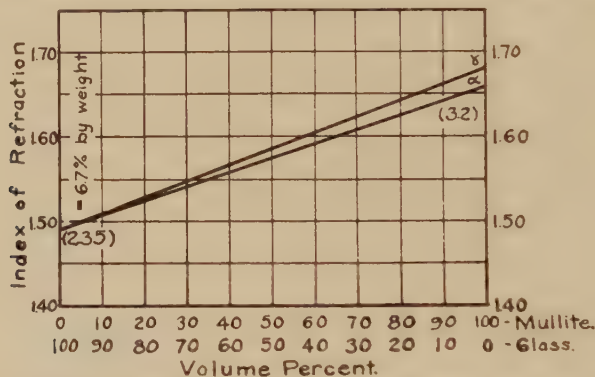


FIG. 13. PER CENT OF MULLITE DEVELOPED IN SILICEOUS BLOCK.

The parallel growth of labradorite crystals indicates that it is a reaction product between glass and refractory.

(C) A block that had broken loose from the bridge and was clogging the flow hole. Much glass had traveled past this block. It is more or less siliceous. (Supplied by Mr. Ross.)

(1) White layer.

Mullite was found together with an aluminous glass which has an index 1.492. The index of the aggregate is 1.50. By similar calculation, it corresponds to 5% by volume or 6.7% by weight of mullite. (Fig. 13).

(2) Brown layer.

Some mullite and labradorite were found with a feldspar glass (index=1.508).

(3) Tank glass.

Index of tank glass is 1.505.

A photomicrograph of the interface is shown in Figs. 14a and 14b.

In order to establish the composition of the brown glass, a chemical analysis was made. The sample was prepared from a vertical surface chipped off the block from the refining end of a tank making a rather soft glass. The chipped pieces were then

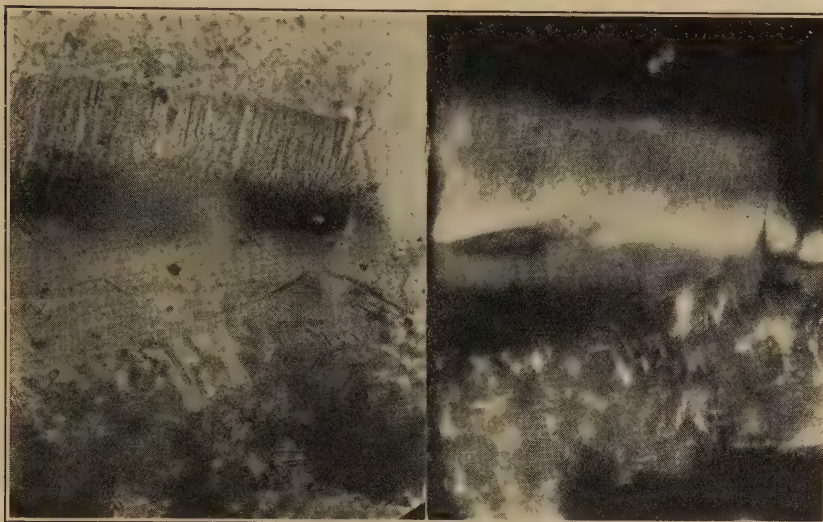


FIG. 14a.

FIG. 14b.

FIG. 14a. SECTION SHOWING INTERFACE OF SAMPLE C. NOTE THE LARGE CRYSTALS OF MULLITE IN THE GLASS MATRIX SHOWING SIGN OF SOLUTION. $\times 250$ DIAMETERS.

FIG. 4b. SAME AS FIG. 14a. CROSSED NICOLS.

ground on both sides down to a fairly clear glass as is ordinarily done in making thin sections. This is powdered for chemical analysis. The microscope reveals very few crystals in this sample. It is essentially a glass. The analysis gives:

SiO_2	63.81
Al_2O_3	16.51
Fe_2O_3	1.24
TiO_2	0.52
CaO	3.48
MgO	1.85
Na_2O	11.70
K_2O	0.07
	99.18

Neglecting the Fe_2O_3 and TiO_2 this corresponds to a molecular formula,



which approaches the composition of a feldspar glass.

The three blocks, A, B, and C, although differing in composition and structure, represent a type not far departed from the theoretical $\text{Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$. In order to study the extreme cases, the following three samples were selected, two highly siliceous samples and one from a tank melting high soda glass. This group is marked by the absence of the brown layer between the tank glass and the refractory, but instead we find a milky white layer in its place.

(D) A highly siliceous soft burned block which has seen service in a bottle glass tank. This was located in the side wall at the level of bottom of tank. (Supplied by Mr. Ross.)

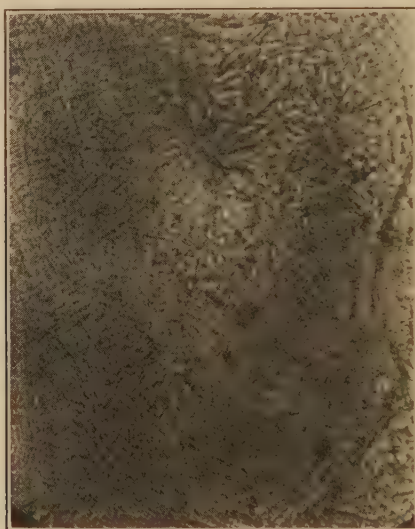


FIG. 15. CRISTOBALITE CRYSTALS FOUND IN THE MILKY WHITE LAYER OF SAMPLE D. NOTE THE FERN PATTERN STRUCTURE. $\times 250$ DIAMETERS.

(1) Block.

Considerable quartz grains were found with an aggregate which has an average index 1.56. The aggregate is composed of very minute mullite crystals imbedded in a glass matrix (index=1.480).

(2) Milky white layer.

Quartz and cristobalite were found together with a siliceous glass (index=1.498). The cristobalite acquires a fern pattern

structure as shown in the photomicrograph. (Fig. 15). The majority of the cristobalite crystals are isotropic and have an index 1.485.

(3) Tank glass.

Index of tank glass is 1.505.

A photomicrograph of the interface is shown in Figs. 16a and 16b.

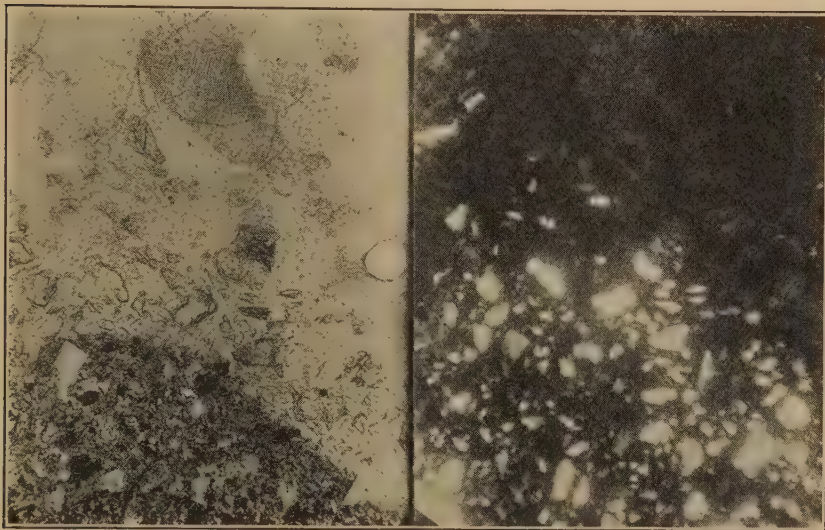


FIG. 16a.

FIG. 16b.

FIG. 16a. SECTION SHOWING INTERFACE OF SAMPLE D. NOTE THE FERN PATTERN CRISTOBALITE CRYSTALS AT THE TOP. QUARTZ GRAINS ARE FAIRLY ROUNDED SHOWING THE EFFECT OF SOLUTION. $\times 60$ DIAMETERS.

FIG. 16b. SAME AS FIG. 16a. CROSSED NICOLS.

(E) A clay placed between used bottom blocks and side wall blocks to level up the surface of the old bottom blocks to match the side wall blocks. It received no burning except that received in the tank. It contains approximately 95% SiO_2 . (Supplied by Mr. Ross.)

(1) Block.

Considerable quartz and some clay aggregate (index=1.57) were found with an interstitial glass (index=1.492).

(2) Milky white layer.

Cristobalite and some quartz were found with a siliceous glass which has an index 1.498.

(3) Tank glass.

Index of tank glass is 1.508.

(F) An aluminous block in a tank making a rather soft glass

and in which the last batch contained a very high soda content. (Supplied by Mr. Ross.)

(1) Block.

Mullite and some residual quartz were found together with an interstitial glass (index=1.508). The aggregate has an average index 1.54.

(2) Milky white layer.

Mullite and a feldspar crystal were found together with a glass which has an index 1.502. The optical properties of this feldspar crystal are as follows:

Biaxial and positive.

$$\alpha = 1.553$$

$$\gamma = 1.558$$

Two cleavages were observed, the extinction angle on one is 3° and on the other is 12° .

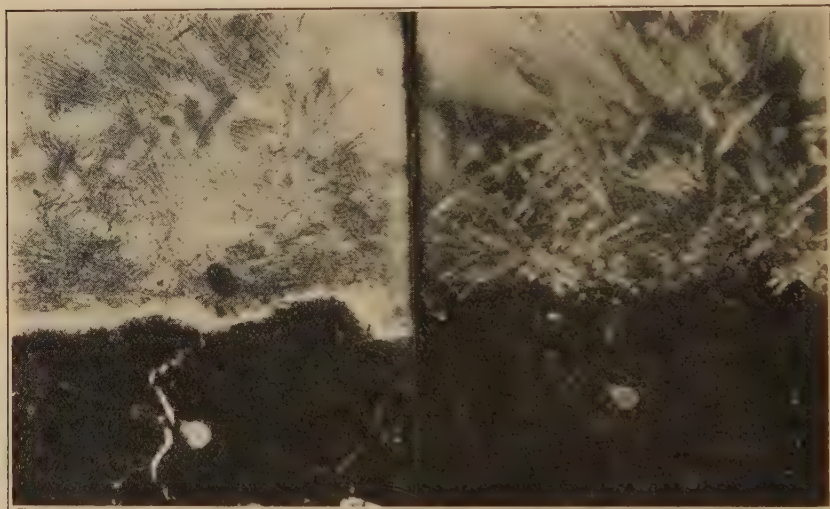


FIG. 17a.

FIG. 17b.

FIG. 17a. SECTION SHOWING INTERFACE OF SAMPLE F. NOTE THE FAN-SHAPED ANDESINE CRYSTALS AT THE TOP. THE DARK SECTION IS THE REFRACTORY. $\times 250$ DIAMETERS.

FIG. 17b. SAME AS FIG. 17a. CROSSED NICOLS.

This is identified as andesine with an approximate composition $\text{Ab}_{55}\text{An}_{45}^{47}$ i. e., 55 mol.% albite and 45 mol.% anorthite.

(3) Tank glass.

The index of the high soda glass is 1.518.

A photomicrograph of the interface is shown in Figs. 17a and 17b.

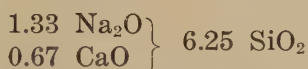
⁴⁷ A. N. Winchell, *El. of Optical Mineralogy*, Pt. II. 279

INTERPRETATION OF THE DATA

Let us consider first from the standpoint of phase rule. We have a glass, e. g., a commercial soda-lime glass. A typical composition will be something like this:

SiO ₂	75.0
Al ₂ O ₃	0.8
Fe ₂ O ₃	0.04
CaO+MgO	7.5
Na ₂ O	16.5
K ₂ O	trace

Neglecting the Al₂O₃ and Fe₂O₃, it can be represented by the molecular formula,



This glass is brought in contact with the refractory, essentially a clay substance whose composition can be represented by Al₂O₃·2 SiO₂. Without taking into consideration any of the impurities we have already a fairly complicated system composed of Na₂O, CaO, Al₂O₃ and SiO₂. Only part of this system has been touched. The ternary system CaO-Al₂O₃-SiO₂,⁴⁸ the revised sys-

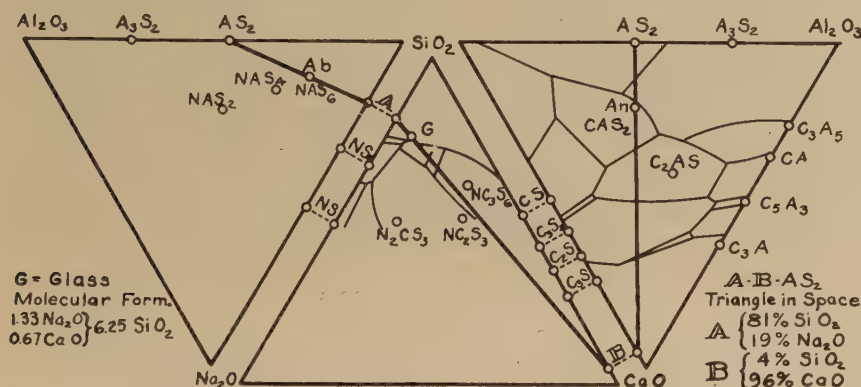


FIG. 18. SYSTEM Na₂O-CaO-Al₂O₃-SiO₂ (WEIGHT PER CENT).

tem Al₂O₃-SiO₂,⁴⁹ the ternary system SiO₂-Na₂SiO₃-CaSiO₃,⁵⁰ and the system albite-anorthite⁵¹ are those that have been thoroughly investigated. These are shown in Figs. 2, 18 and 21.

In Fig. 18, S represents SiO₂, A represents Al₂O₃, N represents

⁴⁸ G. A. Rankin and F. E. Wright, Am. J. Sci. 39, 1-79

⁴⁹ N. L. Bowen and J. W. Greig, J. Am. Cer. Soc. 7, 238-254

⁵⁰ G. W. Morey and N. L. Bowen, J. Soc. Glass Tech. 9, 226-264

⁵¹ N. L. Bowen, Am. J. Sci. 185, 577-599 (1913)

Na_2O and C represents CaO . So A_3S_2 will be mullite and NAS_6 will be albite. Now let us draw a few arbitrary lines. These lines were really drawn after the conclusion had been reached. But for the sake of explanation, the reverse order is a little less complicated. AS_2 represents $\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$, the composition of the refractory, G represents the glass with the composition $1.33 \text{ Na}_2\text{O} : 0.67 \text{ CaO} : 6.25 \text{ SiO}_2$, Ab represents albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$), An represents anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$) and A and B are two arbitrary points.

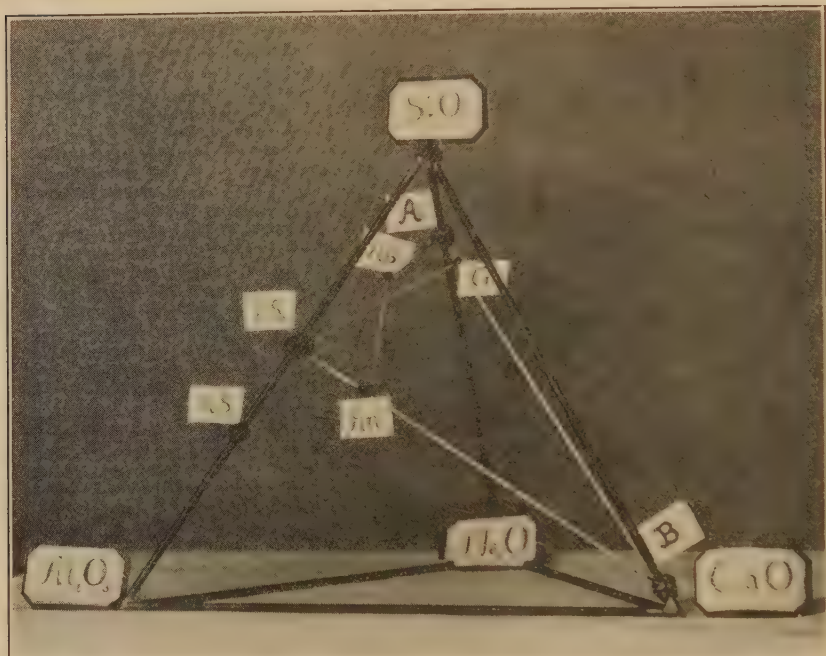


FIG. 19.
SYSTEM $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ SHOWING TRIANGLE A-B- AS_2 IN SPACE.

Draw a line through AS_2 and An, it cuts the SiO_2 - CaO line at B. Then join B and G and extend to A. Join A and Ab and if extended, it should come out to AS_2 . Actually it does not come out at AS_2 but very close to it. By cut-and-try we find a triangle A-B- AS_2 set up in the four component system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. Turning the triangles $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ up until their apices (Al_2O_3) meet, we have a tetrahedron. The triangle A-B- AS_2 in space is shown in Fig. 19. The compositions

of G, An and Ab are slightly off their theoretical values. They are listed below for comparison.

			Theoretical Composition	Calculated from Triangle A-B-AS ₂
Glass		SiO ₂	74.3	74.8
1.33 Na ₂ O	{	CaO	7.4	7.8
0.67 CaO		Na ₂ O	16.3	17.4
Anorthite		SiO ₂	43.3	43.3
CaOAl ₂ O ₃ 2 SiO ₂	{	Al ₂ O ₃	36.6	36.2
		CaO	20.1	20.5
Albite		SiO ₂	68.7	69.8
Na ₂ OAl ₂ O ₃ 6 SiO ₂	{	Al ₂ O ₃	19.5	19.0
		Na ₂ O	11.8	11.2

The triangle A-B-AS₂ laid flat is shown in Fig. 20. The calculation is made from direct measurements. The line albite-anorthite represents the composition of the series of soda-lime feldspars,

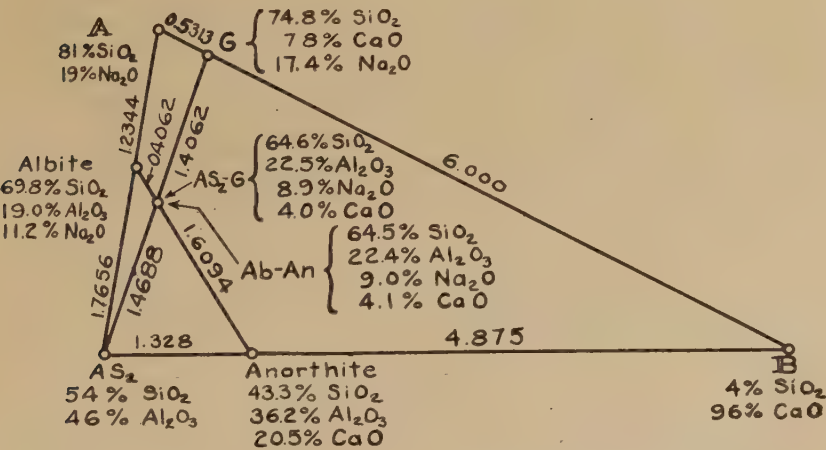


FIG. 20. TRIANGLE A-B-AS₂ IN SPACE (MEASUREMENT IN INCHES).

while the line AS₂-G represents all possible compositions of glasses with clay dissolved in it. The two lines, being on the same plane intersect each other. This is clearly shown by calculating independently the composition of the intersecting point from both lines.

	From line Ab-An	From line AS ₂ -G
SiO ₂	64.5	64.6
Al ₂ O ₃	22.4	22.5
Na ₂ O	9.0	8.9
CaO	4.1	4.0

Now let us consider the system albite-anorthite⁵² as shown in Fig. 21. From the microscopic examination of the brown layer between glass and refractory, we found labradorite present as in the samples A, B and C, although the crystals are not at all abund-

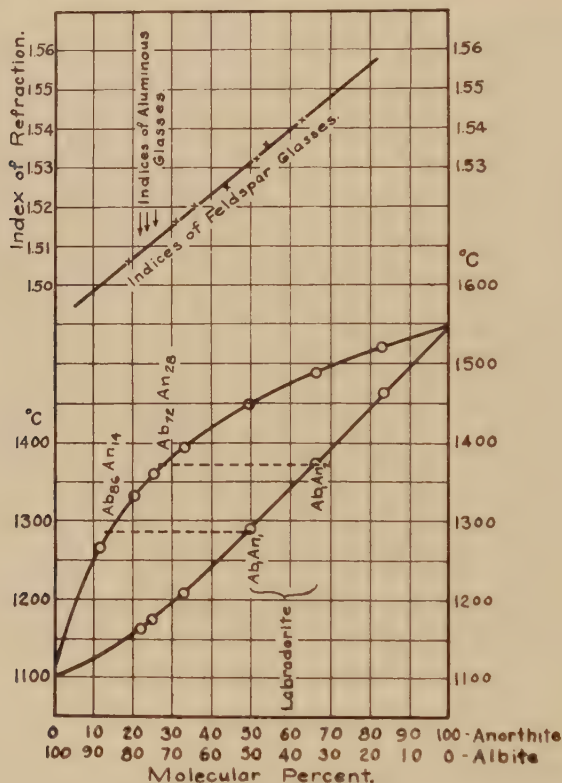


FIG. 21. SYSTEM ALBITE—ANORTHITE
(BOWEN)

ant. Labradorite, being a solid solution is a crystal with variable composition, from Ab_1An_1 to Ab_1An_2 .⁵³ This crystal when it crystallizes out must be in equilibrium with a feldspar glass whose composition is represented on the liquidus at the same temperature. The range of glass composition in equilibrium with labra-

⁵² N. L. Bowen, Am. J. Sci. 185, 577-599 (1913)

⁵³ F. E. Wright, Am. J. Sci. 36, 540 (1913)

dorite is shown in Fig. 21 from $\text{Ab}_{72}\text{An}_{28}$ to $\text{Ab}_{86}\text{An}_{14}$. Convert this range to chemical composition and compare with the compositions of two other glasses obtained from entirely different sources, we have:

	Feldspar Glass in Equilibrium with Labradorite	Intersecting Point of Line Ab-An and Line AS ₂ -G. (Fig. 20)	Analysis of Brown Glass
SiO ₂	66.8-67.8	64.5	63.81
Al ₂ O ₃	20.9-20.2	22.4	16.51
Fe ₂ O ₃			1.24
TiO ₂			0.52
CaO	3.1- 1.5	4.1	3.48
MgO			1.85
Na ₂ O	9.1-10.5	9.0	11.70
K ₂ O			0.07

Taking into account that (1) the analysis of the brown glass is made from one sample, (2) the sample is prepared by grinding off both sides and it is very difficult to locate the boundary between the brown glass and the tank glass, which is responsible for the low Al₂O₃ content and (3) the other two compositions are obtained from entirely theoretical calculations; we may claim quite reasonably that the three compositions represent one and the same glass. This glass is formed by the solution of clay refractory in tank glass. It is one of the glasses that are in equilibrium with the soda-lime feldspars. In other words, the glass resulting from the solution of the clay refractory in commercial glass is of such a character that soda-lime feldspars can crystallize out on cooling.

The commercial glass contains some MgO which also finds its way into the brown glass as shown by the analysis. It probably remains in solution and can be considered as molecular equivalent of CaO in the glass.

There is another set of data which we may consider in this connection, i. e., the refractive indices of the feldspar glasses. In the three samples A, B and C, the brown glasses have indices 1.512, 1.510 and 1.508 respectively as shown in Fig. 21 by three arrows. Deducting from Bowen's data, these glasses correspond to a range of compositions between 22 and 26 mol.% anorthite. Again this comes into the range of composition of glasses which are in equilibrium with labradorite.

In the case of sample F, where the tank melted a high soda batch in the last fire, we find that the glass resulting from the solution of the clay contains more soda and the feldspar in equilibrium

with it has a higher soda content than that of labradorite. The presence of andesine crystals in this sample at the interface of glass and refractory clearly demonstrates the justification of the above explanation.

In the case of samples D and E, where the refractory is very siliceous, we have an entirely different state of equilibrium. This high silica content of the refractory will render the glass resulting from the solution of refractory in tank glass more siliceous. Considering it as a feldspar glass, its composition will be shifted toward the albite end since albite has six molecules of SiO_2 while anorthite has only two. Bowen⁵⁴ has pointed out the difficulty in crystallizing artificially such high soda feldspars. There is little chance for them to crystallize out as feldspars from this glass. But as the silica content is increased beyond its saturation point, silica will separate out. This is shown by the presence of cristobalite crystals in the milky white layer in these samples where highly siliceous refractory was in contact with the tank glass.

Now let us study Fig. 18 a little more carefully. In the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, the field of anorthite is quite a large one, covering a range of compositions from 35% to 75% SiO_2 . Anorthite melts congruently and its composition is inside the field. Albite also melts congruently, and if we consider from the ternary system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$, it must have a field no matter how small it may be. The plagioclase feldspars form a series of solid solutions whose compositions are represented by the straight line joining the compositions of albite and anorthite; and the compositions of all the liquids which are in equilibrium with the feldspars will be represented by an irregular frustrum inside the tetrahedron $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ with the field of albite in the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ as one end and the field of anorthite in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ as the other.

When glass comes in contact with refractory, we get a glass of a feldspar composition. If the composition of the clay differs little from the theoretical $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and the glass approaches the commercial soda-lime type, we shall find the equilibrium established similar to that found in the samples A, B, C and F. A soda-lime feldspar (labradorite in samples A, B and C and andesine in sample F), crystallizes out from the feldspar glass which constitutes the reaction rim between tank glass and refractory. This glass formed by the solution of clay refractory in commercial soda-lime glass will almost certainly have a composition inside the above mentioned frustrum and will be of the feldspar type. But if we have

⁵⁴ N. L. Bowen, *Am. J. Sci.* 185, 584 (1913)

a refractory with extremely high silica content, say, 80-90% as in the case of samples D and E, the resulting glass from solution of refractory in tank glass will be highly siliceous. Since the high soda members of the plagioclase feldspar series cannot crystallize out under ordinary conditions, an increase in silica will naturally result in the crystallization of silica as cristobalite.

In the first part of this investigation, mullite content in burned clays was determined. The aluminous clay burned to cone 28 contains about 46% mullite, while the siliceous clay burned to cone 23+ contains about 14%. The crystals developed are fairly large grains, but those found in samples burned in a commercial kiln to cone 11-12 are too small for optical measurements. It is well known that on heating kaolin to about 900°C. an exothermic reaction occurs which is associated with the dissociation of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ into amorphous mullite and silica. These forms of mullite and silica have a higher potential for chemical reaction and consequently less resistance to the solution in glass. The development of mullite in the samples fired to cone 12 is not any farther than the amorphous state and they are of no major importance in considering the resistance of refractory to glass corrosion. The formation of mullite upon heating a "pure" clay is very slow but the presence of fluxes such as iron, titanium and the alkalies, even in very small per cent, found in most clays appears to exert a real influence on hastening the formation of mullite at a lower temperature. But this argument cannot be carried too far. The action of soda-lime glass on refractory is indeed favorable to the growth of mullite crystal as shown by the existence of the white porcelainous layer between the glass and the refractory. But here another factor comes in. The glass is more than a flux, it is a solvent. It not only exists in enormous quantity in comparison to the interface, but it is also in constant motion in the case of glass tanks. The refractory comes in contact with a continuous flow of glass which is not in equilibrium with the refractory. A solution takes place and the result is a layer of intermediate glass which has a feldspar composition. The feldspars and cristobalite identified in the interface of the samples examined are devitrification products. At the glass melting temperature, they probably exist as a liquid. They crystallize out on cooling.

When the feldspar glass becomes saturated with alumina and silica, the solution of the block will be materially slowed up. This feldspar glass and refractory will be in equilibrium with each other. It is the excess alumina which is dissolved over and above that required to form the feldspar molecules, which is the mullite form-

ing factor. Any change affecting the equilibrium will immediately change the state of affairs and cause a new equilibrium to be set up. A rise in temperature in the tank will result in the lowering of the viscosity of the feldspar glass and it will diffuse into the tank glass much more rapidly than at a lower temperature. A faster flow of the tank glass will bring the feldspar glass in contact with more fresh glass and alumina and silica are given to the tank glass with the balance supplied by the refractory. Consequently more alumina and silica will go into solution and corrosion of the refractory will be accelerated.

AUTOBIOGRAPHY

I, Kai-Ching Lu, was born in Hupeh, China, September 28, 1903. My early education was under private tutorship, and was followed by four year's attendance at the Nankai Middle School, Tientsin, China. My undergraduate work was taken in the Meiji College of Technology, Japan. I graduated with honor from the Meiji College of Technology in 1923, received the degree of Kogakushi in Applied Chemistry and also received the Imperial Award. I came to the United States in 1923 and began my graduate work in Ceramics at the University of Illinois. In 1925 I entered The Ohio State University to continue my graduate work in Ceramics. In the winter of 1925 I received the degree of Master of Science from The Ohio State University. In the year 1926-27 I was University Scholar in Ceramics and in the year 1927-28 I held the Joint Cooperative Glass Fellowship, endowed by the Federal Glass Company, Columbus, Ohio, and the Findlay Clay Products Company, Washington, Pennsylvania, during which time I completed the requirements for the degree of Doctor of Philosophy.

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